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(54) PROCESS FOR THE PREPARATION OF ALKYL-GUANIDINE SALTS

(71) We, SÜDDEUTSCHE KALKSTICKSTOFF-WERKE A.G., or 8223 Trostberg Oberbayern, Germany, a Joint Stock Company organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a process for the preparation of an alkyl - guanidine salt from an alkyl - amine, an aliphatic carboxylic acid and cyanamide.

In U.S. Patent Specification No. 3,004,065, there is described a process for the preparation of alkyl - guanidine salts in aqueous solution from alkylamines containing more than 10 carbon atoms in the alkyl radical, salts of these amines, cyanamide and the acids upon which the amine salts are based. The reaction conditions are stated to include the maintenance of a temperature of 95 to 100°C. and a pH value of at least 9. In the case of this process, for the achievement of an acceptable yield, it is of decisive importance that the cyanamide solution used is very pure with regard to the absence of ferric ions. However, even when observing all of the stated conditions, there is only achieved a maximum yield of 80%, referred to the amount of amine used, or of 52%, referred to the amount of cyanamide used, there being employed a considerable excess of cyanamide, as well as an excess of acid, referred to the amine used. A particular disadvantage of this known process is the long period of reaction, which is said to be 3.5 hours.

Furthermore, from U.S. Patent Specification No. 3,383,408, there is known a process for the preparation of alkyl - guanidine salts from alkylamines, carboxylic acids and an aqueous cyanamide solution in which the starting materials are said to be reacted in substantially equimolar amount at a temperature of about 70—150°C. The period of reaction in this process is as much as 5 hours and the yields obtained of 31.5—73% are also unsatisfactory.

However, in the specific Examples, equimolar ratios of the starting materials are certainly not employed and the cyanamide is used in almost double the stoichiometric amount, referred to the amine. Therefore, in this Patent Specification, the use of a large molar excess of cyanamide or of a considerably reduced amount of amine is indicated as being especially advantageous. Water and alcohols are stated to be suitable reaction media.

The problem forming the basis of the present invention is to provide an economic process, which is substantially more simple to carry out, for the preparation of alkyl guanidine salts from alkylamines, aliphatic car - boxylic acids and cyanamide, which process overcomes the above-mentioned disadvantages of the known processes.

Thus, according to the present invention, there is provided a process for the preparation of an alkyl guanidine salt from an alkylamine containing more than 10 carbon atoms in the alkyl radical, an aliphatic carboxylic acid, which preferably contains up to 5 carbon atoms, and cyanamide in substantially equimolar amounts at a temperature of 80—170°C., preferably of 100—150°C., wherein the cyanamide is added to a melt of the alkylamine and aliphatic carboxylic acid, the reaction being carried out, without the use of a solvent, in the melt within a period of 3—30 minutes.

The cyanamide can be used not only in the form of a solid product but also in the form of a more than 50% aqueous solution or slurry. When adding an aqueous form of the cyanamide, i.e. a cyanamide solution or aqueous cyanamide slurry, it is necessary to prevent substantial amounts of water from getting into the melt. According to a preferred embodiment of the process according to the present invention, the cyanamide is, therefore, added in the form of a more than 50% aqueous solution or slurry with the use of a vacuum and at such a rate that, at the

selected temperature, evaporation of the water takes place practically immediately. The addition of solid cyanamide to the amine salt melt preferably takes place before the melt has reached the reaction temperature. In this way, a good mixing up of the reaction components is ensured at the commencement of the reaction.

An important feature of the process according to the present invention is the length of the period during which the reaction components are heated at the stated temperature. In the case of a period of heating of less than 3 minutes, the reaction is incomplete. When the period of heating exceeds 30 minutes, then a noticeable decomposition of the alkyl - guanidine salt formed takes place. Longer periods of reaction are necessary when the cyanamide is added in the form of a solution, as expulained above, whereas when the cyanamide is added in solid form, it is preferred to use shorter reaction times within the abovementioned range.

The reaction temperature and the period of heating influence one another in that, in the case of the higher temperatures within the stated limits, only the shorter heating times within the stated limits are required. It is preferable to use reaction temperatures between 100 and 150°C. In any case, however, it is necessary to heat to a temperature at which the reaction mixture is present in molten form.

The starting materials are used in molar relationship. The yields which can be achieved by means of the process according to the present invention are between 90 and 96%, referred to the amount of amine or cyanamide employed as starting material. A variation of the molar ratios of the reaction components, such as has been stated in the literature as being advantageous, for example, the addition of 1.2 mole of cyanamide per mole of amine or acid or a slight excess of acid, referred to the amount of amine or cyanamide, has a disadvantageous influence on the degree of reaction in the case of the process according to the present invention. Surprisingly, we have found that the yield is generally reduced by the amount of which the reaction components exceed the molar ratio. Thus, if an excess of cyanamide or of acid is used, the degree of reaction of the amine is decreased and not increased.

If desired, the process according to the present invention can be carried out continuously, for example, in a flow-through tube.

It is of especial advantage that the process according to the present invention is independent of alterations of the pH value of the melt, as well as of the degree of purity of the starting materials. Thus, for example, the presence of ferric ions in the cyanamide used does not exert an undesirable influence on the course of the reaction.

The products obtained by the process according to the present invention can be used, for example, depending on their chemical constitution, as algicides, fungicides or wetting agents.

The following Examples are given for the purpose of illustrating the present invention:—

Example 1

Into an open vessel equipped with a stirrer, which vessel can be heated and cooled, there are placed 50 parts by weight dodecylamine, which is then mixed with 16.2 parts by weight of glacial acetic acid. The dodecylamine acetate which forms is melted at 70°C. The temperature is further increased and at about 80°C., 12.2 parts by weight of cyanamide (95%) are introduced. The mole ratio of dodecylamine : acetic acid : cyanamide is 1 : 1 : 1. Heating is continued until the reaction mixture has reached a temperature of 100—105°C. The temperature slowly increases due to the exothermic reaction. Upon reaching 130°C., the increase of temperature is broken off by cooling the reaction mixture and then drops to 115°C. The total reaction time is 5 minutes. Thereafter, the melt, which is not very viscous, is run off. There are obtained 78.4 parts by weight of a melt which solidifies in crystalline form and contains 90.0% dodecyl - guanidine acetate. Thus, the yield is 90% calculated on the dodecylamine or on the cyanamide used.

Example 2

In a manner analogous to that described in Example 1, 50 parts by weight of dodecylamine are melted with 20 parts by weight of propionic acid and at 80°C., 11.9 parts by weight of 97% cyanamide, mixed with 1.2 parts by weight of water, are introduced. The reaction proceeds exothermally above 105°C. The increase in temperature is interrupted at 130°C. by cooling and the reaction mixture is subsequently maintained at 110°C. The total reaction time is 30 minutes. After running off the melt, there are obtained 82.2 parts by weight of product, which solidifies in crystalline form and contains 89.7% dodecyl - guanidine propionate. The yield is 90.0%, calculated on the dodecylamine or on the cyanamide used.

Example 3

50 parts by weight of dodecylamine are heated with 16.2 parts by weight of glacial acetic acid to 110—115°C. and, within a period of 10 minutes and while maintaining this temperature, 11.8 parts by weight of cyanamide are added dropwise in the form of a 50% solution. During the addition of the cyanamide solution, the reaction mixture is heated to 130°C., with the application of the vacuum of a water jet pump, and thereafter

again cooled to 115°C. The reaction time, after termination of the addition of the cyanamide, is 15 minutes. There are obtained 78.6 parts by weight of melt with a content of 88.5% dodecyl - guanidine acetate, corresponding to a yield of 89.5%, calculated on the dodecylamine or on the cyanamide used.

EXAMPLE 4

50 parts by weight of oleylamine are melted with 11.2 parts by weight of glacial acetic acid at 90—95°C., 8.0 parts by weight 98% cyanamide are introduced and the mixture is heated to 130°C. Thereafter, the reaction mixture is cooled to 110°C. After a total reaction time of 15 minutes, the honey-coloured melt is poured out, whereupon it solidifies in crystalline form within a short period of time. There are obtained 69.2 parts by weight of product with an oleyl - guanidine acetate content of 91.2%.

EXAMPLE 5

50 parts by weight of distearylamine are melted with 5.75 parts by weight of glacial acetic acid at 100°C. and thereafter 4.1 parts by weight of 98% cyanamide are introduced. The reaction mixture is heated to 130—140°C., only a very weak exothermic reaction taking place. For completion of the reaction, the reaction mixture is further heated to 150°C. since the melt already begins to solidify at 140°C. After a total reaction time of 15 minutes, there are obtained 59.9 parts by weight of distearyl-guanidine acetate with a purity of 96.1%. The yield is 96%, calculated on the amine or cyanamide used.

EXAMPLE 6

50 parts by weight of oleylamine are mixed with 8.6 parts by weight of 100% formic acid and 8.0 parts by weight of 98% cyanamide are introduced at 90°C. The reaction proceeds with slight foaming, the temperature thereby increasing. At 130°C., the temperature increase is broken off by cooling. The melt is subsequently maintained for 12 minutes at 110—115°C. There are obtained 66.6 parts by weight of a product with a salve-like consistency which has an oleyl - guanidine formate content of 75%. The content in the same as the yield because the reaction components are used in a mole ratio of 1:1:1.

EXAMPLE 7

50 parts by weight of oleylamine are melted with 13.9 parts by weight of propionic acid (99%) and, at 85°C., are mixed with 8.0 parts by weight of 98% cyanamide. With further heating, the temperature of the reaction mixture is brought to 130°C. (the reaction is less vigorous than in the case of formic or acetic acid) and subsequently maintained for a further 10 minutes at 115°C. Upon cooling, the product solidifies to give a wax-like mass. The yield is 71.8 parts by weight, containing 91.6% oleyl - guanidine propionate. The yield is also 91.6% since the starting materials are used in molar ratio.

WHAT WE CLAIM IS:—

1. A process for the preparation of an alkyl - guanidine salt from an alkylamine containing more than 10 carbon atoms in the alkyl radical, an aliphatic carboxylic acid and cyanamide in substantially equimolar amounts at a temperature of 80—170°C., wherein the cyanamide is added to a melt of the alkylamine and aliphatic carboxylic acid, the reaction being carried out, without the use of a solvent, in the melt within a period of 3 to 30 minutes.

2. A process according to claim 1, wherein the cyanamide is added in the form of a more than 50% aqueous solution or slurry with the use of a vacuum at such a rate that, at the selected temperature, the water evaporates practically immediately.

3. A process according to claim 1, wherein solid cyanamide is added to the amine salt melt at a temperature below the reaction temperature.

4. A process according to any of the preceding claims, wherein the aliphatic car - boxylic acid contains up to 5 carbon atoms.

5. A process according to any of the preceding claims, wherein the reaction is carried out at a temperature of 100—150°C.

6. A process according to any of the preceding claims, wherein the process is carried out continuously.

7. A process according to claim 1 for the preparation of an alkyl - guanidine salt, substantially as hereinbefore described and exemplified.

8. Alkyl - guanidine salts, whenever prepared by the process according to any of claims 1—7.

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